An evaluation of the density functional approach in the zero order regular approximation for relativistic effects: Magnetic interactions in small metal compounds

Belanzoni, P.; van Lenthe, E.; Baerends, E.J.

published in
Journal of Chemical Physics
2001

DOI (link to publisher)
10.1063/1.1345509

document version
Publisher's PDF, also known as Version of record

An evaluation of the density functional approach in the zero order regular approximation for relativistic effects: Magnetic interactions in small metal compounds

Paola Belanzoni
Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

Erik van Lenthe and Evert Jan Baerends[a)]
Theoretical Chemistry Department, Free University, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

(Received 17 October 2000; accepted 12 December 2000)

The performance of the density functional approach in the relativistic zero order regular approximation for the evaluation of electron spin resonance (ESR) parameters in small metal compounds has been evaluated critically by comparison with experimental data and available theoretical results for 22 linear molecules, characterized by a $^2\Sigma$ electronic ground state. For most of the molecules studied the calculated magnetic parameters are in good ($\boldsymbol{A}$ tensors) or reasonable ($\boldsymbol{g}$ tensors) agreement with experiment. Effects of spin-orbit coupling and spin polarization on the calculated hyperfine interaction are investigated. These two effects can only be evaluated separately, since the present method does not allow us to take spin-polarization effects into account in spin-orbit coupled density functional calculations. However, while spin-polarization effects are important for all the molecules investigated, spin-orbit effects are non-negligible only for the molecules containing heavier metal atoms. The ESR parameters, evaluated using different ''standard'' exchange-correlation potentials, have only shown little dependence on the specific functional. Direct relativistic contributions to the hyperfine parameters are often large, especially for the heavier metals, but also ''secondary'' contributions to the ligand hyperfine parameters can be large if the ligand is bound to a heavy element. © *2001 American Institute of Physics.*
[DOI: 10.1063/1.1345509]

I. INTRODUCTION

Electron spin resonance (ESR) spectroscopy is an important tool in experimental studies of the electronic structure of systems containing unpaired electrons and of the influence of the molecular environment on it. A large amount of ESR data is now available for transition metal complexes, stable organic radicals, transient reaction intermediates, solid state and surface defects. However, the interpretation of the experimental spectra in order to extract this kind of information is not always straightforward, and can be greatly improved by theoretical calculations. Hyperfine parameters have been computed recently for a relatively small set of transition metal complexes by various methods. In particular, a number of density functional theory (DFT) studies on transition metal hyperfine parameters have appeared, using the local spin density approximation, generalized gradient approximations (GGA), and several hybrid functionals.[1–3] Reasonable agreement between theory and experiment for the ESR parameters ($\boldsymbol{g}$ and $\boldsymbol{A}$ tensors) has been found, provided that a sufficiently large basis set is employed. Munzarová and Kaupp[3] systematically studied the hyperfine interaction in a number of small $3d$ transition metal complexes. They showed that none of the functionals they tested performed well for all complexes. However, with the computationally much more demanding coupled cluster method they could get good results. In these studies relativistic effects or spin-orbit effects have not been included or have been estimated by rough methods. Further systematic studies are therefore needed in order to judge the ability of the available DFT approaches to describe the ESR parameters for heavy metal systems. Such a systematic study has recently been performed by Patschkovskii and Ziegler,[4] who calculated the $\boldsymbol{g}$ tensors of a series of d^1 transition metal complexes, and found them to be in reasonable agreement with experiment. Relativistic effects were taken into account with a quasirelativistic approach, based on the Pauli Hamiltonian. However, it is well known that the Pauli Hamiltonian is not bounded from below. One way to avoid variational collapse is the direct perturbation theory approach proposed by Rutkowski[5] and Kutzelnigg.[6] Another solution, which is used in this paper, is the use of the zero order regular approximated (ZORA) Hamiltonian,[7–10] which is bounded from below.[11] A different variationally stable approximate relativistic method developed for atomic and molecular calculations by Hess[12] uses the Douglas–Kroll transformation.[13] Also fully relativistic *ab initio* and DFT calculations of molecular properties are increasingly used. Although there exists extensive literature on fully relativistic atomic and solid state calculations of hyperfine interactions, Ref. 14 is one of the few examples where fully relativistic calculations were reported for the evaluation of molecular hyperfine interactions.

a)Electronic mail: baerends@chem.vu.nl

In this paper, we present a critical validation study of the density functional approach using the ZORA method[7–10] for relativistic effects, including a series of small (diatomic and triatomic) metal compounds. This method has been previously applied in the study of neutral atoms Cu, Ag, and Au, of some small test molecules NO_2, HCO, and TiF_3, and of some paramagnetic clusters consisting of five or seven atoms of the group IB metals.[15,16] The calculated ESR parameters were in good agreement with experimental results, thus presenting the DFT ZORA approach as a promising tool in the theoretical evaluation of the magnetic interactions in paramagnetic molecules. Within this approach, it is possible to treat the relativistic effects at the scalar relativistic level or with the inclusion of the spin-orbit operator. The only limitation is due to the fact that it is not yet possible to include simultaneously spin-polarization effects and spin-orbit coupling, i.e., in the spin-orbit coupled equation only spin-restricted density functionals are available, while in the scalar equation also spin-unrestricted density functionals can be used. As a result, the spin-orbit effects and the spin-polarization effects can only be evaluated separately, but at this stage it is interesting to establish their relative importance, and thus to get a feeling of their magnitude for the series of considered metal compounds.

The selection of the molecules used in the present study has been determined mainly by the availability of experimental data on small systems, which have a well-resolved hyperfine structure for the metal and, if possible, also for the ligands. For all the systems, the ESR parameters have been taken from condensed-phase and/or gas-phase measurements. Two different trapping sites, namely inert-gas (Ar or Ne) matrices, are involved. Environmental effects, both structural and electronical, thus have to be expected, influencing the values of the hyperfine parameters and, as a consequence, we cannot aim at a better agreement with experiments than about 10%–15%. Besides, the computed geometrical structures and the corresponding hyperfine parameters do not include any vibrational corrections, which together with the experimental error bars in the structure and hyperfine parameters, contribute to the uncertainties in the comparison between calculation and experiment. In more detail, the considered molecules are ZnH, CdH, HgH, ZnF, CdF, HgF, ZnAg, CdAg, HgAg, ZnCN, CdCN, HgCN, ScO, YO, LaO, BO, AlO, GaO, InO, BS, PdH, and RhC. They are all neutral and characterized by a $^2\Sigma$ electronic state. The σ orbital containing the unpaired electron ranges from covalent to largely ionic, and exhibits various types of s,p,d hybridization. Therefore these molecules represent simple model systems that can be used to test the performance of our methods for the intricate bonding patterns that occur, for instance, in complexes of these metals.

II. COMPUTATIONAL AND METHODOLOGICAL DETAILS

Molecular structures used in the calculations were taken from experiment where available or have otherwise been optimized in unrestricted Kohn–Sham calculations with Becke's gradient correction to the exchange part of the potential[17] and Perdew's gradient correction to the correlation[18,19] included self-consistently. The bond lengths used for all the considered molecules are reported in Table I, where a specification of the experimental or optimized nature of the values is also given. For the InO bond distance, we used the value as used in Ref. 20 (1.877 Å). Geometry optimizations were performed by holding all electrons in the variational space and including relativistic effects in the scalar ZORA approximation. All calculations, both single-point and geometry optimization, were performed using the Amsterdam Density Functional (ADF) program.[21–23] In the ADF code, molecular orbitals are expanded in terms of Slater type orbitals (STOs) and the one-electron Kohn–Sham equations are solved self-consistently using highly efficient numerical techniques.[24] The Vosko, Wilk, and Nusair parametrization[25] of the exchange and correlation energy of the homogeneous electron gas[26] was employed in the local density approximation. Various nonlocal corrections to the exchange and correlation potentials have been included in different calculations, in order to investigate their performance for metal and ligand ESR hyperfine coupling constants. The GGAs for exchange of Becke[17] (denoted Becke88), and of Perdew (both the one denoted PW86x, the correction advocated in 1986 by Perdew–Wang,[27] and the one denoted PW91x, the correction proposed in 1991 by Perdew–Wang[28]) were combined with the corrections for correlation of Perdew (both the one denoted Perdew86, the correction presented in 1986 by Perdew,[18,19] and the one denoted PW91c, the correction of Perdew–Wang 1991[28]), and with LYP, the Lee–Yang–Parr 1988 correction for correlation.[29] The spin unrestricted approach has been applied in order to investigate the spin-polarization effects.

Relativistic effects have been taken into account by the ZORA approach of the Dirac equation. The regular expan-

TABLE I. Bond distances used in the calculations.

MX(Y)	M–X (Å)	X–Y (Å)
ZnH	1.595[a]	···
CdH	1.781[a]	···
HgH	1.766[a]	···
ZnF	1.799[b]	···
CdF	2.014[b]	···
HgF	2.077[b]	···
ZnAg	2.550[b]	···
CdAg	2.727[b]	···
HgAg	2.801[b]	···
ZnCN	1.963[b]	1.167[b]
CdCN	2.180[b]	1.168[b]
HgCN	2.181[b]	1.168[b]
ScO	1.668[a]	···
YO	1.788[a]	···
LaO	1.826[a]	···
BO	1.204[a]	···
AlO	1.618[a]	···
GaO	1.744[a]	···
InO	1.877[c]	···
BS	1.609[a]	···
PdH	1.529[a]	···
RhC	1.613[a]	

[a]Experimental value, Ref. 46.
[b]Optimized bond distance. This work.
[c]Same value as used in Ref. 20.

sion, which leads to the ZORA Hamiltonian, remains valid even for a Coulombic potential. Both the scalar relativistic (SR) approach, which employs the single point group symmetry and includes only the so-called scalar relativistic corrections, and the spin-orbit approach, which solves the spin-orbit coupled equations and uses double-group symmetry, have been applied. In all relativistic calculations, scalar as well as spin orbit, the relativistic atomic core densities and the relativistic atomic potentials have been generated with the auxiliary program DIRAC[30] for fully relativistic Dirac calculations. The ZORA formalism requires special basis sets, primarily to include much steeper core-like functions. The basis sets we used in our molecular calculations can be described as follows: for each atom we employed a triple-ζ all-electron Slater-type orbital basis, quadruple ζ for the valence orbitals, together with four polarization or diffuse functions. The exponents of these STOs were fitted to numerical scalar relativistic ZORA orbitals. To obtain high accuracy extra 1*s* STOs with high exponents were added to make a total of five 1*s* STOs for cadmium and silver and six 1*s* STOs for mercury. These functions with large exponents are needed because for *s* orbitals in the (SR) ZORA and Dirac calculations the wave function has a weak singularity for $\mathbf{r}\rightarrow 0$.[16] Of course, even after the addition of extra compact 1*s* functions, the basis set is not complete and a small error remains. The region near the nucleus is important for the hyperfine interaction, since for small *r* the corresponding operator behaves effectively as an r^{-2} potential for *s* electrons in the (regular) relativistic case. For example, for mercury the remaining basis set incompleteness error can be estimated for a point charge (and point magnetic dipole) to be approximately 5%.

In this respect it may also be important to consider the use of a more realistic finite size of the nucleus, instead of a point nuclear model as we employed in our calculations, which has large effects on the wave function for small *r*. These effects have been investigated by Zhang and Pyper in Ref. 31 using numerical atomic Dirac–Fock calculations. They found that for the neutral copper, silver, and gold atoms, the use of a finite nucleus instead of a point nucleus leads to a decrease in the calculated hyperfine structure constants of 0.7%, 2%, and 13%, respectively. For mercury we can predict that this effect is probably in the same order of magnitude as for gold.

Spin-orbit coupled equations within the ZORA approximation are used for the evaluation of the $\boldsymbol{g}$ tensor, which parametrizes the Zeeman interaction, and of the hyperfine $\boldsymbol{A}$ tensor, which parametrizes the interaction between the (effective) electronic spin of the paramagnetic molecule of interest and a magnetic nucleus in the molecule. The $\boldsymbol{A}$ tensor is also calculated in nonrelativistic and scalar relativistic calculations. The method used here is described in detail in Refs. 15 and 16, where one also can find how the problem of gauge dependence was solved by using gauge including atomic orbitals. For many systems the spin-orbit coupling is usually the most important factor for shifting the $\boldsymbol{g}$ tensor components away from the free electron value g_e. On the $\boldsymbol{A}$ tensor its effect is often small, but can sometimes be significant. In the latter cases, the $\boldsymbol{A}$ tensor is calculated by means of second order perturbation theory[32–35] or is roughly estimated by means of a semiempirical approach following Abragam and Pryce[36] for the inclusion of spin-orbit coupling. In the ZORA spin-orbit coupled equation, the spin-orbit coupling is taken into account variationally, so that simple first order perturbation theory is needed for the effect of the magnetic nucleus. Use of only spin-restricted density functionals can be made in these equations, since a simple method to include both spin-polarization effects and spin-orbit coupling in a density functional calculation is not yet available. Therefore, the effect of spin polarization on the hyperfine interactions is only included in our nonrelativistic and scalar relativistic calculations without spin-orbit coupling.

TABLE II. Mulliken population analysis of the singly occupied σ orbitals of all the compounds considered.

MX(Y)	orbital	M ns (%)	M np_σ (%)	X (%)
				H $1s$
ZnH	8σ	42	29	29
CdH	11σ	42	27	32
HgH	15σ	31	24	44
				F $2p_\sigma$
ZnF	10σ	70	13	15
CdF	13σ	69	11	19
HgF	17σ	55	9	31
				Ag $5s$
ZnAg	17σ	19	15	66
CdAg	20σ	20	14	66
HgAg	24σ	11	11	79
				CN 5σ
ZnCN	12σ	56	25	18
CdCN	15σ	58	20	21
HgCN	19σ	45	19	32
				M $(n-1)d_\sigma$
ScO	9σ	84	7	8
YO	12σ	87	6	7
LaO	15σ	86	8	5
				O $2p_\sigma$
BO	5σ	62	28	5
AlO	7σ	44	17	32
GaO	10σ	28	17	48
InO	13σ	28	17	48
				S np_σ
BS	7σ	47	34	13
			Pd $4d_\sigma$	H $1s$
PdH	10σ	35	38	26
			Rh $4d_\sigma$	C $2p_\sigma$
RhC	12σ	56	11	27

III. RESULTS AND DISCUSSION

A. Electronic structure calculations

Before entering the discussion of the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors, presented in the following sections, it is useful to give a general comment on the electronic structure of the investigated molecules. They are all $^2\Sigma$ radicals, having the unpaired electron in a σ molecular orbital (MO). Among them we can recognize different sets of compounds on the basis of the different nature of the singly occupied MO. The composition of the singly occupied σ orbital of all the calculated molecules is shown in Table II, using a Mulliken population

analysis, which is available in the ADF program. This Mulliken method makes use of the atomic orbitals that are employed to describe the singly occupied molecular σ orbital. The overlap population of two atomic orbitals is divided half and half between the two corresponding atomic orbital populations. As is well known, this Mulliken method depends greatly on the basis sets used, especially for large basis sets (see for example Ref. 37). We therefore chose only to show the Mulliken population analysis based on the calculation where a double-zeta basis set was used. In these calculations the spin restricted scalar relativistic ZORA method was used. Due to the limitations mentioned before this Mulliken population analysis can only give a semiquantitative understanding of the calculated results. On the other hand, it enables us to understand the trends in the results in a relatively simple picture.

One set of molecules consists of the group 12 $(ns)^2$ atoms Zn, Cd, Hg, which are bound to atoms (or to a ligand) with one electron in a σ atomic orbital (AO) or in a MO, like H $(1s)$, F $(2p_\sigma)$, Ag $(5s)$, CN (5σ), and the antibonding MO will be singly occupied. These singly occupied MOs are not degenerate or nearly degenerate with other orbitals and therefore we expect little deviation from the free-electron g_e value. Higher in energy we find empty π orbitals, which mainly consist of np_π character of the Zn, Cd, or Hg atoms. When the ''ligand'' is Ag these π orbitals also contain considerable Ag $5p_\pi$ character.

The second set of molecules are the oxides of the group 3 $(np)^1$ atoms, B, Al, Ga, In (one sulfide, BS), with the unpaired electron in a σ orbital with ns, np_σ hybrid character on the group 3 atom and $2p_\sigma$ character on O (or $3p_\sigma$ character on S). The orbital will be ns,O-$2p_\sigma$ antibonding, and np_σ,O-$2p_\sigma$ bonding. A clear trend in the composition of this singly occupied orbital that can be observed in Table II is the increase in the oxygen $2p_\sigma$ character and the decrease in the metal np_σ character going down the group, in agreement with a relative lowering of the ns so that it becomes energetically closer to the O-$2p$ and has a larger gap with the np_σ.

Important for the $\boldsymbol{g}$ tensor calculations is the highest fully occupied π orbital, since it is close in energy to the singly occupied σ orbital. This orbital has mainly oxygen $2p_\pi$ character, with some contribution from the metal np_π.

In the unrestricted calculations for GaO and InO the special situation is found that the highest occupied α σ orbital is lower in energy than the highest occupied α and β π orbitals, whereas the corresponding empty β σ orbital remains higher in energy than those π orbitals. The α σ orbital is so stabilized due to the unrestricted functional used in these calculations; in the restricted case, the expected order of the orbitals can be found where the singly occupied ns,O-$2p_\sigma$ antibonding σ orbital is higher in energy than the nonbonding (actually slightly np_π,O-$2p_\pi$ bonding) π orbital.

In the free atom comparison method (FACM) the experimental hyperfine interaction parameters are used to estimate the atomic character of the unpaired electron. Knight *et al.*[38,20] used this method to estimate the atomic orbital character of the singly occupied molecular σ orbital of BO, AlO, GaO, and InO. These FACM predictions reproduce the bonding trend that is shown in Table II for this series of metal oxide radicals: going from BO to InO the oxygen $2p_\sigma$ character increases and the metal ns valence character decreases. However, the magnitudes do not exactly match our results. This is not surprising in light of the approximate nature of the FACM method and the limitations of the Mulliken population analysis, which was used for the results in Table II.

A third set of molecules is represented by the group 13 (Sc, Y, La) oxides, with the electron in an nonbonding σ orbital. Table II shows that this orbital is mostly the valence s orbital of the metal with only small contributions of p and d and virtually no oxygen character. For the $\boldsymbol{g}$ tensor calculation the lowest unoccupied molecular orbitals (LUMOs), which are orbitals of δ symmetry, are not important, since these will not mix in the unpaired spinor in a spin-orbit coupled calculation. Slightly higher in energy than the LUMOs, is an empty level of π symmetry, which is important in the $\boldsymbol{g}$ tensor calculations. For ScO and YO this orbital has mixed metal $(n-1)d_\pi$ and metal np_π character. For LaO this empty π orbital has mainly metal $5d_\pi$ and metal $4f_\pi$ character.

Electronic structure and nuclear hyperfine calculations have been previously performed for this set of molecules by Knight *et al.*[2] The computational methods they employed were unrestricted Hartree–Fock, unrestricted density functional with Becke's three-parameter exchange functional, and the gradient corrected Lee–Yang–Parr correlation functional (UB3LYP) and restricted open-shell Hartree–Fock with configuration interaction singles. An electronic structure comparison with their results shows that there is agreement with respect to the nature of the singly occupied σ orbital, namely that it is almost entirely localized on the metal atom.

In addition we calculated PdH and RhC molecules, which have the unpaired electron in a σ orbital of Pd $4d_{z^2}$, $5s$, and H $1s$ character and Rh $4d_{z^2}$, $5s$, and C $2p_z$ character, respectively. Table II shows that for PdH the metal $4d_\sigma$ contribution in the unpaired electron is much larger than for RhC. In PdH there is a fully occupied π orbital, which lies close in energy to the singly occupied σ orbital. This π orbital, which is important in the $\boldsymbol{g}$ tensor calculations, can be described almost purely as a palladium $4d_\pi$ orbital. In the $\boldsymbol{g}$ tensor calculations for RhC the low lying empty π orbital is of importance, which consists of rhodium $5p_\pi$ (14%), $4d_\pi$ (27%), and carbon $2p_\pi$ (59%) character.

B. *g* tensor analysis

In Table III results are given for the g values of all the molecules we investigate, comparing them with the experimental values, where available.[39,20,2] For each of the molecules studied the experimental $g_\parallel$ and $g_\perp$ values demonstrated the expected characteristics for a radical in a $^2\Sigma$ electronic state experiencing small spin-orbit coupling effects, that is all g values are close to g_e. In particular, the parallel component of the $\boldsymbol{g}$ tensor, $g_\parallel$, is close to g_e, and only in a few cases does it deviate more when spin-orbit coupling is not negligible, such as in the Hg compounds, GaO, InO, and PdH. In those molecules the negative deviation of $g_\parallel$ from g_e $(\Delta g_\parallel = g_\parallel - g_e)$ is nicely reproduced by the

TABLE III. Results of restricted relativistic ZORA spin-orbit coupled calculations for **g** tensor components of the considered compounds and experimental data available.

		$g_\parallel$	$g_\perp$
ZnH	spin orbit	2.0019	1.9774
	exp[a]	2.0003	1.9852
CdH	spin orbit	1.9999	1.9306
	exp[a]	1.9970	1.9524
HgH	spin orbit	1.9723	1.7505
	exp[a]	1.976(2)	1.8280
ZnF	spin orbit	2.0020	1.9955
	exp[a]	2.002(1)	1.996(1)
CdF	spin orbit	2.0014	1.9809
	exp[a]	2.001(3)	1.985(2)
HgF	spin orbit	1.9883	1.9362
	exp[a]	1.993(1)	1.961(1)
ZnAg	spin orbit	2.0020	1.9805
	exp[a]	2.0025	1.9905
CdAg	spin orbit	2.0010	1.9510
	exp[a]	2.0014	1.9711
HgAg	spin orbit	1.9919	1.8585
	exp[a]	1.9958	1.9136
ZnCN	spin orbit	2.0020	1.9869
CdCN	spin orbit	2.0008	1.9619
	exp[a]	⋯	1.9681
HgCN	spin orbit	1.9839	1.8651
	exp[a]		1.8789
ScO	spin orbit	2.0022	2.0024
	exp[b]	2.0018	2.0018
YO	spin orbit	2.0021	2.0029
	exp[b]	2.0016	2.0021
LaO	spin orbit	2.0016	1.9960
	exp[b]	2.000(4)	1.999(2)
BO	spin orbit	2.0022	1.9998
	exp[c]	2.0020	2.0006
AlO	spin orbit	2.0020	2.0031
	exp[c]	2.0020	2.0011
GaO	spin orbit	1.9963	1.9139
	exp[c]	1.9990	1.9680
InO	spin orbit	1.9570	1.7248
	exp[c]	1.975(3)	1.810(2)
BS	spin orbit	2.0018	1.9899
	exp[a]	2.0016	1.9942
PdH	spin orbit	1.9746	2.2971
	exp[a]	1.965(2)	2.2932
RhC	spin orbit	2.0003	2.0526
	exp[a]	2.0039	2.0541

[a]Experimental values taken from Ref. 39.
[b]Experimental values taken from Ref. 2.
[c]Experimental values taken from Ref. 20.

calculation. The perpendicular component of the $\boldsymbol{g}$ tensor, $g_\perp$, generally deviates more from g_e, in particular for the heavy element cases, like Hg compounds, GaO, InO, PdH, and RhC, and usually with negative $\Delta g_\perp$, except experimentally for the last two molecules (PdH and RhC). The trends are nicely reproduced by the calculations, although the negative $\Delta g_\perp$ is not always quantitatively reproduced. The cases with an experimentally clear positive $\Delta g_\perp$ (PdH and RhC) are also quantitatively correctly reproduced with the calculations.

For a deeper understanding of these observations we can look at the unpaired electron that results from the spin-restricted spin-orbit coupled calculations. For these molecules, which all have a Kramers doublet ground state, the calculation without magnetic field gives two degenerate spinors, which are eigenfunctions of j_z ($j_z = l_z + s_z$) with eigenvalues $j_z = +1/2$ and $j_z = -1/2$, respectively. These two spinors, connected to each other by time-reversal symmetry, have mainly σ character, with a little mixing due to spin-orbit coupling of π character. In Refs. 15 and 16 it is shown how the parameters of the effective spin Hamiltonian with effective spin $\tilde{\boldsymbol{S}} = 1/2$ are calculated using only the two degenerate spinors. For these molecules the calculated $g_\parallel$ is almost exactly equal to g_e times the amount of σ character in the calculated spinors. Since the sum of the σ and π character in a spinor is equal to 1, it is not difficult to understand why in the calculations $g_\parallel$ is always lower than g_e. At the same time this means that the calculated $\Delta g_\parallel$ is a measure for the calculated π character of the unpaired electron. The $\Delta g_\perp$ is not that easily interpreted; it greatly depends on the exact composition of the σ and π character of the spinor.

For the first set of molecules which contain one group 12 metal (MX, with M=Zn, Cd, Hg and X=H, F, Ag, CN), the situation is still relatively simple. If we treat spin-orbit coupling as a perturbation, we can start with the scalar relativistic situation in which the unpaired electron is in a σ orbital. Spin-orbit coupling is now strongest between the σ orbital and the low lying empty π orbital, which has mainly metal np_π character. The coupling matrix element between these orbitals arises from the spin-orbit coupling between the metal np_σ character of the σ orbital and the metal np_π character of the empty π orbital. The spinor with $j_z = +1/2$ is thus approximately

$$\begin{pmatrix} as(\mathrm{M}) + bp_z(\mathrm{M}) + c\sigma(\mathrm{X}) \\ d(p_x + ip_y)(\mathrm{M}) \end{pmatrix}. \tag{1}$$

This means that the g values can be approximately calculated as

$$g_\parallel \approx g_e(a^2 + b^2 + c^2), \tag{2a}$$

$$g_\perp \approx g_\parallel - 2g_e bd. \tag{2b}$$

The relative magnitudes of the a,b,c coefficients originate from the σ orbital and their signs will reflect the antibonding between metal ns and X σ and bonding between metal np_σ and X σ in that molecular orbital. The relative sign of b and d, however, is determined by the spin-orbit coupling. In this case the spin-orbit coupling with the empty metal np_π orbital will stabilize the lower lying σ orbital. As in the comparable case of the stabilized $p_{1/2,1/2}$ atomic orbital arising from spin-orbit coupling in a degenerate p manifold, the b and d coefficients have the same sign. This means that the calculated $g_\perp$ will be lower than g_e. In the notation of Weltner[39] this is a situation where there is interaction between the ground $^2\Sigma$ state and a $^2\Pi_r$ excited state.

Table II shows that the metal np_σ character ($\approx b^2$) is roughly the same for a given ligand, whether the metal is Zn, Cd, or Hg. Also the orbital energy differences between the singly occupied σ orbital and lowest unoccupied π orbital in

the scalar relativistic calculations are not very different for a given ligand, whether the metal is Zn, Cd, or Hg. On the other hand, the spin-orbit interaction between np_σ and np_π increases from Zn to Cd to Hg, which will result in higher π character ($\approx 2d^2$) of the unpaired electron. This explains qualitatively the larger $\Delta g_\perp$ values going from the zinc compounds to the cadmium compounds to the mercury compounds.

For a given metal, there is some correlation between the differences in the $\Delta g_\perp$ values and the np_σ character ($\approx b^2$) of the unpaired electron. This can be understood, since in the simple model of Eq. (2) $\Delta g_\perp$ is proportional to b. For a more quantitative analysis of the calculated values given in Table III one should also include the effects due to the metal d character and possible ligand p character in the singly occupied σ and lowest unoccupied π orbital, the orbital energy differences between these two orbitals, possible overlap effects, and the interaction with other π orbitals.

The calculated g values for PdH can also be understood in a relatively simple manner. In contrast to the previous case, where the occupied $(n-1)d_\pi$ level is too far below the singly occupied orbital to have an important spin-orbit coupling with the latter, now spin-orbit coupling is strongest between the metal nd_σ character of the σ orbital and the highest occupied π orbital, which has mainly metal nd_π character. In this case the spinor with $j_z=+1/2$ is approximately

$$\begin{pmatrix} as(\mathrm{Pd}) + bd_{z^2}(\mathrm{Pd}) + cs(\mathrm{H}) \\ d(d_{xz} + id_{yz})(\mathrm{Pd}) \end{pmatrix}, \tag{3}$$

and the g values can be approximately calculated as

$$g_\parallel \approx g_e(a^2 + b^2 + c^2), \tag{4a}$$

$$g_\perp \approx g_\parallel - 2\sqrt{3} g_e bd. \tag{4b}$$

The spin-orbit interaction in this case destabilizes the σ orbital to form the spinor of Eq. (3), and b and d have opposite sign, as in the destabilized $d_{5/2,1/2}$ spinor. As a corollary the calculated $g_\perp$ will be higher than g_e. In the notation of Weltner[39] there is interaction between the ground $^2\Sigma$ state and a $^2\Pi_i$ excited state.

Next we consider the oxides of the group 3 atoms, B, Al, Ga, In, and one sulfide BS. Here we have strong spin-orbit interaction of the singly occupied σ and the highest fully occupied π orbital, which both have mixed metal and ligand character. In the notation of Weltner[39] we still have an interaction between the ground $^2\Sigma$ state and a $^2\Pi_i$ excited state. However, as we will see, this does not automatically mean that a positive $\Delta g_\perp$ is calculated. The spinor with $j_z=+1/2$ is approximately

$$\begin{pmatrix} as(\mathrm{M}) + bp_z(\mathrm{M}) + cp_z(\mathrm{X}) \\ d(p_x + ip_y)(\mathrm{M}) + e(p_x + ip_y)(\mathrm{X}) \end{pmatrix} \tag{5}$$

and the g values are approximately calculated as

$$g_\parallel \approx g_e(a^2 + b^2 + c^2), \tag{6a}$$

$$g_\perp \approx g_\parallel - 2g_e bd - 2g_e ce. \tag{6b}$$

The values of b and c are almost the same as in the singly occupied σ orbital in the scalar relativistic calculation, since there is only small mixing of π character. The bonding in this orbital between the metal p_z and X p_z orbitals implies that b and c have opposite signs. From Table II approximate values for b^2 and c^2 can be obtained. The π character of the calculated spinor is almost solely due to the admixture by the spin-orbit coupling of the highest fully occupied π orbital. This means that the relative magnitude and sign of d and e are the same as in this bonding π orbital, where d and e have the same sign, and where e is roughly twice as large as d. For BO, AlO, and BS, the largest contribution to the coupling matrix element comes from the spin-orbit interaction matrix element between the O(S) p_σ character of the singly occupied σ orbital and the O(S) p_π character of the highest fully occupied π orbital. The spin-orbit interaction is destabilizing in this case, thus c and e have the opposite sign as in a $p_{3/2,1/2}$ spinor. Using the arguments previously given, based on the relative phases between c and b and between e and d that follow from the chemical bonding interactions, this means that b and d have the same sign. For the calculation of $g_\perp$ both ce and bd are of equal importance, but they are of opposite sign, making it hard to predict beforehand what the sign of $\Delta g_\perp$ will be. If we assume that the ratio between d and e is almost the same for BO, AlO, and BS, we can qualitatively understand the sign of $\Delta g_\perp$. Here it should be added that the sign of $\Delta g_\perp$ for AlO does depend on the size of the basis set used. For AlO the absolute value of $\Delta g_\perp$ is relatively small.

For GaO and InO the situation is different. Here spin-orbit interaction is strongest between the (relatively small) metal p_σ character of the singly occupied σ orbital and the (relatively small) metal p_π character of the highest fully occupied π orbital. Again the spin-orbit interaction destabilizes the unpaired electron orbital (spinor), but now this means that b and d have opposite signs. Using the arguments given above this means that c and e have the same sign. Now both in the singly occupied σ orbital as well as in the fully occupied π orbital the oxygen p character is larger than the metal p character. This means that ce is larger in magnitude than be, and since ce is positive, from Eq. (6) it follows that $\Delta g_\perp$ is negative.

For RhC spin-orbit interaction is strongest between the (relatively small) rhodium d_σ character of the singly occupied σ orbital and the (relatively small) rhodium d_π character of the lowest unoccupied π orbital. The spinor with $j_z=+1/2$ is approximately

$$\begin{pmatrix} as(\mathrm{Rh}) + bd_{z^2}(\mathrm{Rh}) + cp_z(\mathrm{C}) \\ d(d_{xz} + id_{yz})(\mathrm{Rh}) + e(p_x + ip_y)(\mathrm{C}) \end{pmatrix} \tag{7}$$

and the g values are approximately calculated as

$$g_\parallel \approx g_e(a^2 + b^2 + c^2), \tag{8a}$$

$$g_\perp \approx g_\parallel - 2\sqrt{3} g_e bd - 2g_e ce. \tag{8b}$$

Spin-orbit interaction stabilizes the unpaired electron orbital (spinor), which means that b and d have the same sign as in a $d_{3/2,1/2}$ spinor, and if one neglects the ce term one would expect a negative $\Delta g_\perp$. However, a positive $\Delta g_\perp$ is calculated which is due to the (much) larger carbon p character than metal d character in the orbitals considered. In both orbitals the p and d contributions are antibonding, which

means that b and c have the same sign, and d and e have the opposite sign. Thus ce is negative. It turns out that the absolute value of ce is larger than $\sqrt{3}bd$, which explains the calculated positive $\Delta g_{\perp}$.

The Δg values for the group 13 (Sc, Y, La) oxides are relatively small. This can be understood if we consider that in these molecules the singly occupied σ orbital in the scalar relativistic calculations only has small metal p and d character, and the π orbitals do not lie very close in energy. The unpaired electron resulting from the spin-orbit coupled equation has (small) π character that is due to several π orbitals, both occupied and unoccupied, in the scalar relativistic calculation. We do not give a more quantitative analysis, since it is relatively complicated.

As a general comment on Table III, we note that the calculated values are reasonably close to the experimentally determined values and that the ordering of the g values, i.e., $g_{\perp}$ versus $g_{\parallel}$ is almost always reproduced in the calculations. The errors in the $g_{\perp}$ component are in general larger than those in the $g_{\parallel}$ component and show mostly negative deviation in the calculated values. Systematic errors cannot be found in the $g_{\parallel}$ component, which shows both positive and negative deviations within the different series of compounds.

C. The hyperfine *A* tensor

Results of the theoretical $\boldsymbol{A}$ tensor components are given in Table IV, for all the molecules considered. Experimentally determined A values (rare gas matrix or/and gas phase) are reported for comparison.[39,20,2] The gradient corrected density functional Becke88 Perdew86 has been used in unrestricted relativistic scalar ZORA calculations. The effects due to spin-orbit coupling are therefore neglected, while spin-polarization effects are taken into account.

In the group 12 compounds (MX, with M=Zn, Cd, Hg and X=H, F, Ag, CN) we can, for a given M, consider the variation of the A values along the series of the ligands X and we can check to what extent the trends in the singly occupied orbital composition, shown in Table II, explain the experimental observations. Since the singly occupied molecular orbital (SOMO) is antibonding between the σ AO (or MO) on X and the ns on M, the bonding combination being fully occupied, we expect that with increasing electronegativity of X the bonding orbital becomes more fully σ AO (or MO) of X and the SOMO gets more ns character of M or, in other words, the spin becomes more localized on M. As a consequence, the isotropic hyperfine interaction $A_{\mathrm{iso}}=(2A_{\perp}+A_{\parallel})/3$ should increase. For the dipolar term $(A_{\mathrm{dip}}=(A_{\parallel}-A_{\perp})/3)$, the trend in M np character of the SOMO should be considered.

For the M hyperfine splitting in the series H, F, Ag, CN, we note that the M splittings are rather isotropic, $A_{\parallel}$ and $A_{\perp}$ being quite close. This is in agreement with the large ns and small np content of the SOMO. There is increasing electronegativity of X in the order Ag $<$H$<$CN$<$F as reflected, for instance, in the calculated hyperfine interactions at M. This trend, shown by the scalar unrestricted calculations, is similarly followed by the experimental values (see Table IV). In terms of isotropic contribution to the hyperfine splitting, the expected trend is nicely reproduced: the isotropic A_{iso} value increases with the M ns character of the SOMO, in the order, Ag, H, CN, F. For instance, for Zn the calculated ns character on the metal is 19%, 42%, 56%, and 70% for X=Ag, H, CN, F, respectively, and the corresponding calculated isotropic A_{iso} values are 357, 561, 1045, and 1223 MHz, respectively. A similar trend is found for Cd and Hg. The reason that the calculated A_{iso} values are not exactly proportional to the calculated ns characters of the SOMOs

TABLE IV. Results of unrestricted scalar relativistic ZORA calculations for hyperfine parameters (in MHz) in the compounds and experimental data considered.

MX(Y)		$A_{\parallel}$(M)	$A_{\perp}$(M)	$A_{\parallel}$(X)	$A_{\perp}$(X)
^{67}Zn^{1}H	scalar	603	540	543	543
	exp[a]	⋯	⋯	485	487
^{111}Cd^{1}H	scalar	−3698	−3368	575	578
	exp[a]	4358	3966	515	515
^{199}Hg^{1}H	scalar	7430	6792	736	746
	exp[a]	7790	6608	707	711
^{67}Zn^{19}F	scalar	1250	1210	812	−54
	exp[a]	⋯	⋯	673	143
^{111}Cd^{19}F	scalar	−7833	−7654	831	−139
	exp[a]	⋯	⋯	670	64
^{199}Hg^{19}F	scalar	18415	18085	1408	−387
	exp[a]	22622	21880	1344	195
^{67}Zn^{107}Ag	scalar	371	350	−1296	−1297
	exp[a]	⋯	⋯	1324	1324
^{111}Cd^{107}Ag	scalar	−2322	−2198	−1279	−1280
	exp[a]	2180	1990	1327	1327
^{199}Hg^{107}Ag	scalar	3822	3640	−1517	−1517
	exp[a]	3130	2520	1562	1562
^{67}Zn^{13}CN	scalar	1080	1027	278	240
^{111}Cd^{13}CN	scalar	−6895	−6641	277	236
	exp[a]	7890	7558	⋯	⋯
^{199}Hg^{13}CN	scalar	15543	15032	412	347
	exp[a]	16770	15390	⋯	⋯
^{45}Sc^{17}O	scalar	1970	1910	−21.4	−21.0
	exp[b]	1997	1923	19.6	20.7
^{89}Y^{17}O	scalar	−809	−790	−18.3	−17.9
	exp[b]	791	763	16.8	16.8
^{139}La^{17}O	scalar	3697	3641	−11.2	−9.8
	exp[b]	3724	3630	$<$10	$<$10
^{11}B^{17}O	scalar	1046	961	−54	17
	exp[c]	1082	1000	−43	−7
^{27}Al^{17}O	scalar	722	552	−105	75
	exp[c]	851	682	−98	52
^{69}Ga^{17}O	scalar	1361	995	−155	95
	exp[c]	1736	1356	−145	85
^{115}In^{17}O	scalar	1696	1165	−166	93
	exp[c]	1728	1188	−228	166
^{11}B^{33}S	scalar	838	744	49	−21
	exp[a]	853	767	⋯	16
^{105}Pd^{1}H	scalar	−969	−881	130	117
	exp[a]	867	801	103	106
^{103}Rh^{13}C	scalar	−1087	−1070	90	42
	exp[a]	1113	1089	89	55

[a]Experimental values taken from Ref. 39.
[b]Experimental values taken from Ref. 2.
[c]Experimental values taken from Ref. 20.

has to do with the limitations of the Mulliken population analysis used in Table II.

When looking at the dipolar contribution to the hyperfine splitting, the M np character of the SOMO does not completely agree with the calculated trend. For a given M, the np content of the SOMO increases according to F<Ag<CN<H (see Table II), whereas the calculated (and the experimental) A_{dip} dipolar term increases following the sequence Ag<F<CN<H. For Zn, the calculated dipolar A_{dip} values are 7, 13, 18, and 21 MHz in the order X=Ag, F, CN, H; for Cd, the calculated dipolar A_{dip} values are −41, −60, −85, and −110 MHz, and for Hg 61, 110, 170, 213 MHz, in the same X order. The difference in ordering in the results for X=Ag and F can presumably be ascribed to the qualitative nature of the Mulliken population analysis used in Table II.

Let us consider now the trend in the X hyperfine splitting (hfs) when the metal M is varied in the series Zn, Cd, Hg. We note that changes of X hfs along the ZnX, CdX, HgX series are not so large and particularly for H and Ag the $\boldsymbol{A}$ tensor is very isotropic, as expected from the ligand ns contribution to the SOMO (the Ag $5p$ contribution to the SOMO is very small). For H, the calculated A_{iso} is 543, 577, and 743 MHz in the sequence M=Zn, Cd, Hg and for Ag the same A_{iso} term is −1297, −1280, and −1517 MHz in the same M order. Clearly the results for Zn and Cd are rather comparable but there is an evident change when going to Hg. For F and CN this change is even more striking: for F the calculated $A_{\parallel}$ value is 812, 831, and 1408 MHz in the series M=Zn, Cd, Hg, and for C the calculated A_{iso} is 253, 250, and 369 MHz in the same M series. The ''special'' case of Hg is due to a relativistic effect (see Sec. III F).

Table IV shows that among the four ligands considered, the fluorine $\boldsymbol{A}$ tensor is the most anisotropic. The fluorine $\boldsymbol{A}$ tensor also deviates very much from the 2 to 1 ratio for $A_{\parallel}$ to $A_{\perp}$ expected for a pure p_{σ} electron. On the other hand, there is no evidence of significant fluorine $2s$ contribution to the SOMO. The significant isotropic A_{iso} values of 235, 184, and 211 MHz, in the series M=Zn, Cd, Hg are caused by the spin-polarization effects in the $2s$ and $1s$ F orbitals. The opposite polarizations of inner shells and their relatively large contributions to the contact term have been noted and discussed before.[40–43] The signs of $A_{\parallel}$ and $A_{\perp}$ for F could not be determined from the available experimental data.[44,45] The assumption was made that they are both positive, thus implying that the major contribution to the hyperfine interaction is direct admixture of fluorine $2s$ and $2p_{\sigma}$ orbitals, rather than a spin-polarization mechanism. However, our calculations suggest that $A_{\parallel}$ and $A_{\perp}$ are of opposite sign. As in previous studies on TiF_3,[43] the spin polarization of the inner shells (even the lowest occupied $1s$ shell!) on fluorine is very important, both for the anisotropic and the isotropic parts of the hyperfine tensor.

Finally, Table IV shows that the ^{13}C hfs in the CN ligand series Zn, Cd, Hg compounds is quite isotropic. We can understand this if we consider that the CN 5σ orbital entering the SOMO is localized mainly on the C atom and contains a large contribution from C $2s$ orbital, with minor $2p_{\sigma}$ percentage.

In the group 3 oxides (BO, AlO, GaO, InO, one sulfide BS), the calculated hyperfine interactions are in rather good agreement with experiment, as we can see from Table IV, notably also at the oxygen. Exceptions are represented by the hfs at Ga in GaO and the hfs at O in InO. Of course, for the heavier systems, like InO and GaO, the effect of spin-orbit coupling has to be considered to make definite statements. The calculated M dipolar A_{dip} values, which mainly reflect the M np SOMO content, are very close to the experimental values as shown in Table V, where a comparison with nonrelativistic UB3LYP[20] [or configuration interaction (CI)][38] calculations is also reported. It is interesting to note that for the metal A_{iso} values our method gives better agreement with experiment than the methods used in Refs. 20 and 38.

The larger boron A_{iso} in BO (989 MHz) compared to BS (775 MHz) agrees with the calculated larger boron $2s$ character in BO compared to BS (see Table II). On the other hand, in the group 3 oxide series the oxygen hyperfine split

TABLE V. Comparison between the unrestricted scalar relativistic ZORA calculations, UB3LYP (or CI) calculations and experimental data (neon and argon matrices, gas phase) for hyperfine parameters (in MHz) in the group 3 and 13 oxides.

MX(Y)		A_{iso}(M)	A_{dip}(M)	A_{iso}(X)	A_{dip}(X)
$^{11}B^{17}O$	scalar	989	28	−7	−24
	CI[a]	1080	26	−20	−16
	exp[b](neon matrix)	1033	25	−19	−12
	exp[b](gas phase)	1027.4	27.1	⋯	⋯
$^{27}Al^{17}O$	scalar	609	57	15	−60
	UB3LYP[b]	540	61	9	−65
	exp[b](neon matrix)	766	52	2	−50
	exp[b](gas phase)	738.0	56.4	⋯	⋯
$^{69}Ga^{17}O$	scalar	1117	122	12	−83
	UB3LYP[b]	648	123	2	−89
	exp[b](neon matrix)	1483	127	8	−77
$^{115}In^{17}O$	scalar	1342	177	7	−86
	UB3LYP[b]	523	173	−4	−90
	exp[b](neon matrix)	1368	180	35	−131
$^{45}Sc^{17}O$	scalar	1930	20.0	−21.1	−0.1
	UB3LYP[c]	1878	20.3	−16.9	0.4
	exp[c](neon matrix)	2018(1)	24.7(4)	−20.3(3)	0.4(2)
	exp[c] (argon matrix)	2005(1)	26.3(6)	−18.9(4)	0.7(3)
	exp[c](gas phase)	1947.3	24.8	⋯	⋯
$^{89}Y^{17}O$	scalar	−796	−6.3	−18.0	−0.1
	UB3LYP[c]	−675	−6.3	−12.8	0.2
	exp[c](neon matrix)	−807.5(4)	−9.5(3)	−16.8(2)	0.0(2)
	exp[c] (argon matrix)	−801.(1)	−10.3(7)	−15.1	0.0(3)
	exp[c](gas phase)	−772.4	−9.4	⋯	⋯
$^{139}La^{17}O$	scalar	3660	18.7	−10.3	−0.5
	UB3LYP[c]	2502	13.6	−4.7	−1.2
	exp[c](neon matrix)	3751(5)	29(4)	(−10)	≈0
	exp[c] (argon matrix)	3691(6)	32(5)	(−15)	≈0
	exp[c](gas phase)	3662.1	31.5	⋯	⋯

[a]Theoretical values taken from Ref. 38.
[b]Experimental and theoretical values taken from Ref. 20.
[c]Experimental and theoretical values taken from Ref. 2.

TABLE VI. Results of restricted (*R*) ZORA (including spin-orbit coupling), restricted (*R*) and unrestricted (*U*) scalar relativistic ZORA calculations for hyperfine parameters (in MHz).

MX			$A_{\parallel}$(M)	$A_{\perp}$(M)	$A_{\parallel}$(X)	$A_{\perp}$(X)
$^{67}Zn^{1}H$	spin orbit	*R*	678	600	433	427
	scalar	*R*	676	605	433	428
	scalar	*U*	603	540	543	543
$^{111}Cd^{1}H$	spin orbit	*R*	−4389	−3853	431	428
	scalar	*R*	−4326	−3957	433	431
	scalar	*U*	−3698	−3368	575	578
$^{199}Hg^{1}H$	spin orbit	*R*	10530	8262	533	532
	scalar	*R*	9837	9106	557	559
	scalar	*U*	7430	6792	736	746
$^{67}Zn^{19}F$	spin orbit	*R*	1248	1198	801	−35
	scalar	*R*	1247	1200	796	−23
	scalar	*U*	1250	1210	812	−54
$^{111}Cd^{19}F$	spin orbit	*R*	−7992	−7719	797	−151
	scalar	*R*	−7964	−7756	779	−108
	scalar	*U*	−7833	−7654	831	−139
$^{199}Hg^{19}F$	spin orbit	*R*	20340	19558	1387	−687
	scalar	*R*	20248	19838	1219	−305
	scalar	*U*	18415	18085	1408	−387
$^{67}Zn^{107}Ag$	spin orbit	*R*	393	365	−1282	−1278
	scalar	*R*	392	368	−1281	−1279
	scalar	*U*	371	350	−1296	−1297
$^{111}Cd^{107}Ag$	spin orbit	*R*	−2557	−2346	−1250	−1247
	scalar	*R*	−2528	−2388	−1251	−1249
	scalar	*U*	−2322	−2198	−1279	−1280
$^{199}Hg^{107}Ag$	spin orbit	*R*	4827	4106	−1462	−1459
	scalar	*R*	4570	4356	−1479	−1477
	scalar	*U*	3822	3640	−1517	−1517
$^{67}Zn^{13}C^{14}N$	spin orbit	*R*	1071	1006	257	214
	scalar	*R*	1069	1010	257	215
	scalar	*U*	1080	1027	278	240
$^{111}Cd^{13}C^{14}N$	spin orbit	*R*	−6989	−6603	249	203
	scalar	*R*	−6948	−6672	250	205
	scalar	*U*	−6895	−6641	277	236
$^{199}Hg^{13}C^{14}N$	spin orbit	*R*	16909	15403	344	273
	scalar	*R*	16580	16008	356	289
	scalar	*U*	15543	15032	412	347
$^{45}Sc^{17}O$	spin orbit	*R*	1951	1910	−24.8	−23.6
	scalar	*R*	1952	1912	−24.8	−23.6
	scalar	*U*	1970	1910	−21.4	−21.0
$^{89}Y^{17}O$	spin orbit	*R*	−807	−792	−21.5	−20.4
	scalar	*R*	−811	−798	−21.6	−20.6
	scalar	*U*	−809	−790	−18.3	−17.9
$^{139}La^{17}O$	spin orbit	*R*	3742	3691	−14.5	−13.0
	scalar	*R*	3733	3699	−14.7	−12.7
	scalar	*U*	3697	3641	−11.2	−9.8
$^{11}B^{17}O$	spin orbit	*R*	912	814	−51	9
	scalar	*R*	912	816	−51	9
	scalar	*U*	1046	961	−54	17
$^{27}Al^{17}O$	spin orbit	*R*	814	639	−107	48
	scalar	*R*	813	645	−110	53
	scalar	*U*	722	552	−105	75
$^{69}Ga^{17}O$	spin orbit	*R*	2048	1668	−170	118
	scalar	*R*	2049	1663	−146	69
	scalar	*U*	1361	995	−155	95
$^{115}In^{17}O$	spin orbit	*R*	2966	2400	−221	209
	scalar	*R*	2967	2402	−147	71
	scalar	*U*	1696	1165	−166	95
$^{11}B^{33}S$	spin orbit	*R*	704	596	52	−9
	scalar	*R*	702	600	54	−11
	scalar	*U*	838	744	49	−21
$^{105}Pd^{1}H$	spin orbit	*R*	−997	−996	130	107
	scalar	*R*	−1013	−947	135	119
	scalar	*U*	−969	−881	130	117
$^{103}Rh^{13}C$	spin orbit	*R*	−1077	−1069	91	63
	scalar	*R*	−1077	−1071	94	54
	scalar	*U*	−1087	−1070	90	42

ting is rather anisotropic. As already noticed in Ref. 20, the oxygen $2s$ character in the SOMO is nearly zero for all four MO radicals. Table II shows that going from BO to InO the oxygen $2p_{\sigma}$ character increases. Therefore, the isotropic contribution to the oxygen $\boldsymbol{A}$ tensor is expected to be very small, whereas the dipolar contribution is expected to increase down the group. Actually, this expectation is confirmed by the results reported in Table V. They are in rather good agreement with experiment, except for InO, where the effect of spin-orbit coupling is important (see Table VI).

For group 13 oxides (ScO, YO, LaO), the agreement with experiment is generally good (as shown in Table IV) both for the metal and the oxygen. Since the SOMO can be essentially described as a metal $ns,np_{\sigma},(n-1)d_{\sigma}$ hybrid (see Table II), with a very small oxygen contribution, we expect the oxygen hyperfine splittings to be quite small. Indeed, as shown in Table IV, the O hfs is small in all molecules, with a decreasing trend down the group, and it is also isotropic. This means that, since a single $2p$ unpaired electron on O gives much larger and anisotropic hfs, the very small participation of the oxygen to the SOMO takes place through an *s* orbital, as confirmed by orbital composition analysis. It is evident that these compounds are very ionic, with a quite large negative charge on O, and for all three molecules the unpaired electron resides almost entirely on the metal atom.

Since the SOMO is mostly the valence *s* orbital of the metal, the isotropic term of the metal $\boldsymbol{A}$ tensor is by far larger than the dipolar term, as we can see from Table V. It is interesting to compare our results with the metal and oxygen hyperfine splittings measured in neon and argon matrices in gas phase and calculated by the UB3LYP method. These values are summarized in Table V. For the metal, our method reproduces the A_{iso} experimental value better than the UB3LYP method used in Ref. 2 in all three molecules, while for A_{dip} our results are closer to the UB3LYP values than to the experimental values. It should be noted that relativistic effects are very important for LaO (see Table VIII). These are not included in the UB3LYP calculations reported in Ref. 2.

For the oxygen, again a better agreement of our results with experiment can be found for the A_{iso} value. For the A_{dip} we find very good agreement with experiment, namely that the magnitude of these values is very small (nearly zero) in all cases.

Of course, when we compare calculated values to experiment, the effects of the ''inert'' rare gas matrix should be taken into account. As seen from the metal oxide data shown

in Table V, the matrix A_{dip} parameter for the metal is equivalent to the gas phase measurement within the experimental uncertainty, whereas neon matrix values of A_{iso} for metals exceed the gas phase by approximately 1%–4%. It would appear that the repulsive interactions with the neon matrix atoms cause the electron density to increase in the vicinity of the metal atom and thereby increase the isotropic spin density at the nucleus. Therefore, when comparing the calculated and the experimental neon matrix A_{iso} values, this ''extra'' discrepancy has to be considered.

The last two molecules whose hyperfine splittings we analyze are PdH and RhC. As shown in Table IV, the agreement with experiment is very good, both for the metal and for the ligand. For PdH, which has the unpaired electron in a σ orbital of Pd $4d_{z^2}$, Pd $5s$ and H $1s$ character (see Table II), we expect an isotropic hfs for hydrogen and an anisotropic $\boldsymbol{A}$ tensor for Pd, with a large A_{iso} contribution. This is indeed what can be found in Table II. On the other hand, if the H $1s$ character for PdH of the SOMO is compared to that of ZnH, which is close, one would also expect a similar hydrogen hyperfine interaction, whereas the calculated hydrogen hyperfine interaction in ZnH is much larger than the one in PdH. Again we describe this discrepancy to the limitations of the Mulliken method that was used for the composition of the SOMO in Table II.

For RhC, with the unpaired electron in a σ orbital of mostly Rh $5s$ character (56%) and in addition Rh $4d_{z^2}$, and C $2p_z$ character, the $\boldsymbol{A}$ tensor should be isotropic for the metal and anisotropic for the carbon atom, with a large A_{iso} term for Rh and a considerable A_{dip} term for C. Again, the expectations are confirmed by the data in Table IV.

Of course, we expect that A values are sensitive to the molecular geometry, which could be particularly important in view of the not completely satisfactory results, for instance, for the group 12 atoms (Zn, Cd, Hg) which are bound to fluorine, for which a geometry optimization had to be performed. Therefore, an investigation of the interdependence between structural changes and hyperfine A values should be undertaken. For this purpose, the series of group 3 oxides and BS have been chosen as the most suitable series, since they give reasonable $\boldsymbol{g}$ tensor components and hyperfine parameters with the experimentally determined bond lengths. Geometry optimization calculations have been done on this series, and at the optimized bond lengths $\boldsymbol{g}$ and $\boldsymbol{A}$ tensor calculations have been carried out. By comparing the results to the experimental values, the theoretical bond distances appeared to be reliable for all the compounds considered and, comparing the magnetic property results with the data reported in Table III and IV, neither $\boldsymbol{g}$ tensor components nor the hyperfine parameters showed significant variations. Analogously, we checked that there is a similar small effect of changing the geometries on the magnetic properties in the other compounds by adding 0.01 Å to the optimized bond distances of the group 12 atom fluoride series (ZnF, CdF, HgF). We conclude that the hyperfine $\boldsymbol{A}$ tensor components depend only slightly on the bond lengths in the compounds investigated.

D. Spin-orbit versus spin-polarization effects

In order to assess the relative importance of the spin-orbit and the spin-polarization effects, separate relativistic ZORA calculations have been performed. The reason is that at present these two effects cannot be treated simultaneously in the ADF code, but also we are interested in comparing their contributions in the various series of compounds we investigated. In Table VI results of restricted (R) relativistic ZORA spin-orbit (only spin-orbit effects included), unrestricted (U) relativistic ZORA scalar (only spin-polarization effects included), and restricted (R) relativistic ZORA scalar (spin-orbit and spin-polarization effects not included) calculations for hyperfine parameters in all the series of compounds considered are compared.

For the group 3 oxides (and BS sulfide) we have already seen that the deviations of the $\boldsymbol{g}$ tensors from the free-electron g_e value are small. We may therefore expect a negligible spin-orbit effect on the hyperfine A values. This can be investigated by comparing the spin-orbit restricted and scalar restricted sets of data in Table VI. With the only exception of the A values relative to the oxygen in the InO molecule (and, to a smaller extent, the A values of the oxygen in the GaO) the two sets of data do not show variation on passing from a spin-orbit restricted treatment to a scalar restricted one. On the other hand, when going to a scalar unrestricted approach a substantial change can be found, because of the spin-polarization effects.

Focusing on the group 12 atom series (Zn, Cd, Hg) we note that, for most of these molecules, the largest differences arise between the scalar unrestricted and scalar restricted results. This means that overall the spin-polarization effects are the most important effects in this series. The spin-orbit coupling effects are only non-negligible for the Hg compounds. In particular, for HgH, the Hg $A_{\parallel}$ and $A_{\perp}$ components show a larger variation due to spin-polarization effects but also a non-negligible variation due to spin-orbit effects (see the difference between spin-orbit restricted and scalar restricted data). Besides, while the spin-polarization effects lead the $A_{\parallel}$ and $A_{\perp}$ values closer to the experimental data, although underestimating them, at the same time they worsen the agreement between the calculated and the experimental $\boldsymbol{A}$ tensor anisotropy ($A_{\parallel}-A_{\perp}$). Therefore, the HgH molecule represents a case where both spin-polarization and spin-orbit effects should be taken into account simultaneously, as it is not yet clear how the two effects are related (presumably they are not additive). For HgF, the spin-polarization effects are again the most important, both for the metal and the ligand, but for Hg they give rise to worse agreement with experiment than the spin-orbit results. The fluorine $\boldsymbol{A}$ tensor is more difficult to analyze, since experimentally only the absolute signs of the parallel and perpendicular components are measured. It is interesting to note that considering the fluorine $\boldsymbol{A}$ tensor in HgF for the $A_{\perp}$ component the spin-orbit effects are considerably larger than the spin-polarization effects. Comparing the HgAg molecule spin-orbit and spin-polarization effects, we note that the spin-polarization effects are more important; the largest differences can be observed between the scalar restricted and scalar unrestricted values. However, substantial spin-orbit effects are indicated by the

TABLE VII. Dependence of hyperfine parameters of the diatomic metal fluorides series on the exchange-correlation functional (in MHz).

MX	GGA		$g_\parallel$	$g_\perp$	$A_\parallel$(M)	$A_\perp$(M)	$A_\parallel$(X)	$A_\perp$(X)
$^{67}Zn^{19}F$	Becke88 Perdew86	spin orbit	2.0020	1.9955				
		scalar			1250	1210	812	−54
	PW86x Perdew86	spin orbit	2.0020	1.9960				
		scalar			1198	1158	904	−31
	PW91x PW91c	spin orbit	2.0020	1.9956				
		scalar			1254	1214	803	−49
	PW86x PW91c	spin orbit	2.0020	1.9961				
		scalar			1206	1167	877	−31
	Becke88 LYP	spin orbit	2.0020	1.9957				
		scalar			1237	1196	879	−31
		exp[a]	2.002(1)	1.996(1)	⋯	⋯	673	143
$^{111}Cd^{19}F$	Becke88 Perdew86	spin orbit	2.0014	1.9809				
		scalar			−7833	−7654	831	−139
	PW86x Perdew86	spin orbit	2.0014	1.9815				
		scalar			−7409	−7237	927	−106
	PW91x PW91c	spin orbit	2.0014	1.9813				
		scalar			−7862	−7684	825	−133
	PW86x PW91c	spin orbit	2.0014	1.9815				
		scalar			−7476	−7306	898	−103
	Becke88 LYP	spin orbit	2.0014	1.9813				
		scalar			−7685	−7504	903	−118
		exp[a]	2.001(3)	1.985(2)	⋯	⋯	670	64
$^{199}Hg^{19}F$	Becke88 Perdew86	spin orbit	1.9883	1.9362				
		scalar			18415	18085	1408	−387
	PW86x Perdew86	spin orbit	1.9880	1.9398				
		scalar			17508	17189	1530	−288
	PW91x PW91c	spin orbit	1.9886	1.9376				
		scalar			18586	18257	1400	−376
	PW86x PW91c	spin orbit	1.9883	1.9894				
		scalar			17738	17419	1510	−288
	Becke88 LYP	spin orbit	1.9880	1.9398				
		scalar			18065	17730	1488	−337
		exp[a]	1.993(1)	1.961(1)	22622	21880	1344	195

[a]Experimental values taken from Ref. 39.

difference between the spin-orbit restricted and the scalar restricted data both for the silver *A* values and for the mercury *A* values. As a result, if only spin-polarization effects are included, the silver *A* values are underestimated with respect to the experimental values, while the mercury *A* values are overestimated. Finally, in the HgCN molecule, for both the mercury *A* values and the carbon *A* values, the spin-polarization effects are the largest, but again the spin-orbit effects are also non-negligible.

For group 13 (Sc, Y, La) oxides, all *g* values are close to the free-electron g_e value, thus leading us to expect negligible spin-orbit effects on the hyperfine *A* values. Indeed, Table VI shows that there is very little variation if a comparison is made of the spin-orbit restricted *A* values with the scalar restricted ones, both for the metal and for the oxygen. When going to the scalar unrestricted approach a change can be observed because of the spin-polarization effects, which is rather modest for these compounds.

In the ''special'' molecules PdH and RhC both spin-orbit and spin-polarization effects enter the *A* values for the ligands (H and C) and for Pd, while for Rh only spin polarization affects the *A* values.

E. Performance of different exchange-correlation functionals

Table VII gives the *g* values, and the metal and ligand hyperfine parameters for the three group 12 metal fluoride molecules (ZnF, CdF, HgF) and for the five functionals of this study (Becke88 Perdew86, PW86x Perdew86, PW91x PW91c, PW86x PW91c, and Becke88 LYP combinations) in comparison with experiment. We chose the Zn, Cd, and Hg fluorides because we obtained the ''worst'' results for this series. This investigation focuses on compounds with the SOMO mainly localized on the metal, therefore the spin densities at the ligand nuclei are much smaller than those at the metal nuclei. This places considerable demand on the computational approach to describe the subtle delocalization of spin density to the ligands and the spin-polarization effects. Besides, relativistic effects, considered here by means of the scalar ZORA unrestricted approach, may have a non-negligible influence on the small ligand hyperfine values. Concerning the dependence of the ESR $\boldsymbol{g}$ and $\boldsymbol{A}$ tensor parameters on the exchange-correlation potential, from Table VII it is striking that the difference between these ''stan-

TABLE VIII. Comparison between unrestricted scalar relativistic ZORA and unrestricted nonrelativistic (NR) calculations of hyperfine parameters (in MHz).

MX		$A_{\parallel}$(M)	$A_{\perp}$(M)	$A_{\parallel}$(X)	$A_{\perp}$(X)
$^{67}Zn^{1}H$	scalar	603	540	543	543
	NR	574	512	512	512
$^{111}Cd^{1}H$	scalar	−3698	−3368	575	578
	NR	−3042	−2737	486	487
$^{199}Hg^{1}H$	scalar	7430	6792	736	746
	NR	4098	3595	471	473
$^{67}Zn^{19}F$	scalar	1250	1210	812	−54
	NR	1168	1130	748	−28
$^{111}Cd^{19}F$	scalar	−7833	−7654	831	−139
	NR	−6066	−5905	653	−67
$^{199}Hg^{19}F$	scalar	18415	18085	1408	−387
	NR	8596	8364	695	−89
$^{67}Zn^{107}Ag$	scalar	371	350	−1296	−1297
	NR	289	267	−957	−958
$^{111}Cd^{107}Ag$	scalar	−2322	−2198	−1279	−1280
	NR	−1677	−1546	−890	−890
$^{199}Hg^{107}Ag$	scalar	3822	3640	−1517	−1517
	NR	2314	2121	−902	−903
$^{67}Zn^{13}CN$	scalar	1080	1027	278	240
	NR	1011	959	260	225
$^{111}Cd^{13}CN$	scalar	−6895	−6641	277	236
	NR	−5380	−5148	226	194
$^{199}Hg^{13}CN$	scalar	15543	15032	412	347
	NR	7373	6995	233	201
$^{45}Sc^{17}O$	scalar	1970	1910	−21.4	−21.0
	NR	1959	1901	−20.8	−20.4
$^{89}Y^{17}O$	scalar	−809	−790	−18.3	−17.9
	NR	−716	−699	−16.1	−16.1
$^{139}La^{17}O$	scalar	3697	3641	−11.2	−9.8
	NR	1798	1705	−20.2	−22.7
$^{11}B^{17}O$	scalar	1046	961	−54	17
	NR	1048	963	−54	17
$^{27}Al^{17}O$	scalar	722	552	−105	75
	NR	731	561	−104	75
$^{69}Ga^{17}O$	scalar	1361	995	−155	95
	NR	1354	992	−148	93
$^{115}In^{17}O$	scalar	1696	1165	−166	93
	NR	1568	1065	−150	89
$^{11}B^{33}S$	scalar	838	744	49	−21
	NR	840	746	49	−21
$^{105}Pd^{1}H$	scalar	−969	−881	130	117
	NR	−714	−622	233	228
$^{103}Rh^{13}C$	scalar	−1087	−1070	90	42
	NR	−875	−859	71	16

dard'' functionals is not significant. No functional appears to give superior agreement with experiment; they all perform comparably.

F. Relativistic effects

It is well established that for heavy elements relativistic effects are important for obtaining good agreement with experiment. Therefore we expect that relativistic effects do have an influence on the Ag, Hg, La, In, Pd, Rh (probably also for Cd, Y, and Ga) hyperfine parameters in the corresponding series. Table VIII shows a comparison between the unrestricted relativistic scalar ZORA and the unrestricted nonrelativistic (NR) results for all the compounds considered. These hyperfine parameters are calculated with exactly the same basis set in the relativistic and nonrelativistic case, and with exactly the same points in the numerical integration. This is done in order to ensure a high accuracy in the calculation of the relativistic effects. As expected, the larger relativistic effects are found for the heavier elements previously mentioned. The relativistic results are in closer agreement with the experimental values and are larger than the nonrelativistic results: of about 9% for In, ranging from 65% (in HgAg) to 115% (in HgF) for Hg, ranging from 35% (in ZnAg) to 68% (in HgAg) for Ag, about 105% for La, 40% for Pd, 25% for Rh, and 13% for Y.

The trend in the ligand hyperfine splitting when the metal M is varied in the series Zn, Cd, Hg is investigated in more detail. In the relativistic calculations it was found that when M is Zn or Cd the results are rather comparable, but when M is Hg there is an evident change. Of importance is the relativistic stabilization of the Hg 6*s*, which will increase the Hg 6*s* character in the fully occupied bonding orbital (bonding orbital of Hg 6*s* with the σ AO of X), decrease its character in the SOMO, and hence increase the X σ AO content of the SOMO. The influence of the relativistic effects can be determined by looking at the nonrelativistic unrestricted results for the $\boldsymbol{A}$ tensor components calculated for the group 12 compounds, shown in Table VIII. Indeed, at the NR level the H hfs has no break for the HgH case, with the calculated $A_{\parallel}$ value of 512, 486, and 471 MHz in the sequence M= Zn, Cd, Hg. The same is true for the ligand hfs of the other ligands F, CN, and Ag (see Table VIII). Of course, we are now talking about a ''secondary'' relativistic effect, which is the only relativistic effect for the nonrelativistic atoms H, F, and CN. For Ag there is in addition a primary relativistic effect on the Ag hfs. Similarly, the relativistic ''change of covalency'' effect in the Hg compounds is also present in the total relativistic effect for the Hg hfs, but then of course also direct relativistic effects are large.

Another example where scalar relativistic effects are important for the hyperfine parameters of the ligand is PdH. For this molecule, the relativistic effects on the *A* values for hydrogen are even larger than those for Pd: −44% versus 40%, respectively. Finally, it is interesting to note that there are only two cases where relativistic effects significantly reduce the *A* values with respect to the nonrelativistic calculations, namely in the oxygen hfs of LaO (−45%) and in the H hfs of PdH (−44%).

Thus, significant relativistic contributions, not only direct but also ''secondary,'' to the hyperfine parameters are calculated and their inclusion (even when discussing the ligand hyperfine parameters if the ligand is bound to a heavy element) has to be considered.

IV. CONCLUSION

The present investigation shows the DFT relativistic regular approximation (ZORA) approach to be a promising tool in the quantitative calculation of ESR parameters for metal systems. For a number of small metal molecules, considered as test cases, density functional calculations have been performed for the evaluation of the magnetic interactions. The influence of several effects has been investigated.

Spin-orbit coupling has been taken into account variationally, in self-consistent spin-restricted DFT relativistic ZORA calculations for the $\boldsymbol{g}$ and $\boldsymbol{A}$ tensors. Spin-polarization effects have been included in both scalar relativistic and nonrelativistic calculations for the evaluation of the magnetic hyperfine interaction ($\boldsymbol{A}$ tensor) in order to evaluate the importance of relativistic effects. A comparison between results of restricted relativistic ZORA spin-orbit (only spin-orbit effects included), unrestricted relativistic ZORA scalar (only spin-polarization effects included), and restricted relativistic ZORA scalar (spin-orbit and spin-polarization effects not included) calculations for hyperfine parameters has been carried out with the aim of assessing the relative importance of spin-orbit and spin-polarization effects. At present in the spin-orbit coupled equation only spin-restricted density functionals are available and the simultaneous inclusion of spin-orbit and spin-polarization effects is not possible yet. Our unrestricted scalar relativistic ZORA results are in good agreement with experiment for most of the molecules studied, at least within the experimental uncertainty (1%–4%) and the ''inert'' rare gas matrix effects ($\sim$10%–15%); exceptions are represented by heavier metal systems for which spin-orbit coupling is non-negligible for hyperfine parameters and should be taken into account simultaneously with spin-polarization effects. The importance of spin polarization for the hyperfine parameters has been observed for all molecules. It has been shown that relativistic effects in the calculation of the hyperfine parameters are large not only for the heavy metals but also for the ligands bound to heavy elements due to ''secondary'' effects and their inclusion is important for good agreement with the experimental values, in particular for Hg, Ag, La, Pd, and their corresponding ligands. Scalar relativistic effects increase the A values considerably with respect to the nonrelativistic calculations, except for oxygen in LaO and for hydrogen in PdH, where the relativistic A values are reduced. Different ''standard'' exchange-correlation functionals are used in calculations for hyperfine parameters. They all give close results, thus showing that the choice of such a functional is not critical for the systems investigated. The trends in the singly occupied orbital composition in the compounds studied, analyzed using a Mulliken population method, explain the trends in the experimental and calculated results for ESR parameters in a relatively simple picture. However, the Mulliken method suffers from basis set dependence, notably for very large basis sets, and it can therefore only be used in a qualitative way with preferably modest size basis sets. In the actual calculations of the ESR parameters large all-electron basis sets were used. These are needed to describe the wave function near the magnetic nucleus accurately, which is important for the calculation of the hyperfine interaction. In the future the DFT ZORA approach described above should be extended to treat larger systems, with orbitally degenerate ground states and more than one unpaired electron. It will also be important to take spin polarization in spin-orbit coupled density functional calculations into account.

[1] S. M. Matter and B. J. Doleman, Chem. Phys. Lett. **216**, 369 (1993).
[2] L. B. Knight, Jr., J. G. Kaup, B. Petzoldt, R. Ayyad, T. K. Ghanty, and E. R. Davidson, J. Chem. Phys. **110**, 5658 (1999).
[3] M. Munzarová and M. Kaupp, J. Phys. Chem. A **103**, 9966 (1999).
[4] S. Patschkovskii and T. Ziegler, J. Chem. Phys. **111**, 5730 (1999).
[5] A. Rutkowski, J. Phys. B **19**, 149 (1986).
[6] W. Kutzelnigg, Z. Phys. D: At., Mol. Clusters **11**, 15 (1989).
[7] J. E. Harriman, *Theoretical Foundations of Electron Spin Resonance* (Academic, New York, 1978).
[8] Ch. Chang, M. Pelissier, and Ph. Durand, Phys. Scr. **34**, 394 (1986).
[9] J-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, and A-M. Mårtensson-Pendrill, J. Phys. B **19**, 2799 (1986).
[10] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[11] R. van Leeuwen, E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).
[12] B. A. Hess, Phys. Rev. A **33**, 3742 (1986).
[13] M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).
[14] R. A. Arratia-Pérez and D. A. Case, J. Chem. Phys. **79**, 4939 (1983).
[15] E. van Lenthe, P. E. S. Wormer, and A. van der Avoird, J. Chem. Phys. **107**, 2488 (1997).
[16] E. van Lenthe, A. van der Avoird, and P. E. S. Wormer, J. Chem. Phys. **108**, 4783 (1998).
[17] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).
[18] J. P. Perdew, Phys. Rev. B **33**, 8822 (1986).
[19] J. P. Perdew, Phys. Rev. B **34**, 7406 (1986).
[20] L. B. Knight, Jr., T. J. Kirk, J. Herlong, J. G. Kaup, and E. R. Davidson, J. Chem. Phys. **107**, 7011 (1997).
[21] The Amsterdam density functional program, version ADF 1999.03.
[22] C. Fonseca Guerra, J. G. Snijders, G. te Velde, and E. J. Baerends, Theor. Chem. Acc. **99**, 391 (1998).
[23] L. Versluis and T. Ziegler, J. Chem. Phys. **88**, 322 (1988).
[24] G. te Velde and E. J. Baerends, J. Comput. Phys. **99**, 84 (1992).
[25] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
[26] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[27] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986).
[28] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[29] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).
[30] F. Herman and F. Skilman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1963).
[31] Z. C. Zhang and N. C. Pyper, Mol. Phys. **64**, 963 (1988).
[32] M. H. L. Pryce, Proc. Phys. Soc., London, Sect. A **63**, 25 (1950).
[33] A. J. Stone, Proc. R. Soc. London **271**, 424 (1963).
[34] C. P. Keizers, Ph.D. thesis, Katholieke Universiteit, Nijmegen, The Netherlands, 1974.
[35] P. J. M. Geurts, P. C. P. Bouten, and A. van der Avoird, J. Chem. Phys. **73**, 1306 (1980).
[36] A. Abragam and M. H. L. Pryce, Proc. R. Soc. London, Ser. A **205**, 135 (1951).
[37] F. M. Bickelhaupt, N. J. R. van Eikema Hommes, C. Fonseca Guerra, and E. J. Baerends, Organometallics **15**, 2923 (1996).
[38] L. B. Knight, Jr., J. Herlong, T. J. Kirk, and C. A. Carrington, J. Chem. Phys. **96**, 5604 (1992).
[39] W. Weltner, Jr., *Magnetic Atoms and Molecules* (Van Nostrand Reinhold, New York, 1983).
[40] D. A. Case and M. Karplus, J. Am. Chem. Soc. **99**, 6182 (1977).
[41] J. Weber, A. Goursot, E. Pénigault, J. H. Ammeter, and J. Bachmann, J. Am. Chem. Soc. **104**, 1491 (1982).
[42] P. Belanzoni, M. Gribnau, and E. J. Baerends, J. Phys. Chem. A **103**, 3732 (1999).
[43] P. Belanzoni, E. J. Baerends, S. van Asselt, and P. B. Langewen, J. Phys. Chem. **99**, 13094 (1995).
[44] L. B. Knight, Jr., T. A. Fisher, and M. B. Wise, J. Chem. Phys. **74**, 6009 (1981).
[45] L. B. Knight, Jr., A. Mouchet, W. T. Beaudry, and M. Duncan, J. Mol. Struct. **32**, 383 (1978).
[46] M. E. Radzig and B. M. Smirnov, *Reference Data on Atoms, Molecules, and Ions* (Springer, Berlin, 1985).